Journal of Applied Chemistry
JAC
http://chemistry.journals.semnan.ac.ir

Micro- spherical SnO_2/Zn_2SnO_4: Synthesis, heat treatment and photocatalytic efficiency for decolorization of two dye mixture in wastewater

M. Movahedi[a,*], A. Hosseinian[b], M. Bakhshaei[c], M. Rahimi[a], I. Arshadnia[a]
[a]*Department of Chemistry, Payame Noor University, P.O. Box 19395-3697 Tehran, Iran.*
[b]*Department of Engineering Science, University College of Engineering, University of Tehran, P.O. Box 11365-4563, Tehran, Islamic Republic of Iran.*
[c]*Faculty of Marine Science & Technology, Tehran North Branch, Islamic Azad University, Tehran, Iran.*
Article history:
Received: 31/Jan/2016
Received in revised form: 5/Apr/2016
Accepted: 20/Apr/2016

Abstract
In the present work, a new micro- spherical SnO_2/Zn_2SnO_4 *via* a refluxing method has been synthesized. The heat treatment of the product was carried out at 500 and 900 ºC for 1 h. The sample was characterized by X-ray diffraction (XRD), UV-Vis spectrophotometer and field emission scanning electron microscopy (FE-SEM). The SnO_2/Zn_2SnO_4 sample was formed after heat treatment at 900 ºC for 1h. The average diameter of micro- spheres of about ~2.7 µm were obtained. The photocatalytic activity of the sample by decolorization of two dye mixture- methylene blue (M.B.) and methyl orange (M.O.) was evaluated under UV-Vis. irradiation. The result showed that the SnO_2/Zn_2SnO_4 sample is capable to decolorize (M.B.) and (M.O.) in dye mixture solution.

Keywords: Micro- spherical, SnO_2/Zn_2SnO_4, Photocatalyst.

1. Introduction

Removal of organic pollutants in wastewater is important for environmental protection. One of the main sources of the dye pollutants in waste water is the textile industry. The direct photolysis of organic dye in the natural aquatic environment is difficult. Most of all commercial dyes are usually designed to be light resistant. Therefore, the researchers have been directed towards the investigation of organic dye photodegradation by photocatalysts in aqueous system under UV-Vis. and visible irradiation.

Photocatalyst has been widely applied in the treatment of dye pollutants in wastewater [1-3]. Until now, various kinds of compound materials, such as metal oxide and nanocomposites have been widely used as a photocatalyst [4-8]. Many researchers have been reported the properties of semiconductors depend on their crystal structure, size and morphology [9, 10]. Therefore, achieving high photocatalytic activity is still a challenge. Until now, different methods for synthesis of Zn_2SnO_4 and SnO_2/Zn_2SnO_4 have been reported in literature [11-13].

[*]**.Corresponding author:** *E-mail address:m.movahedi@pnu.ac.ir; Tel.: +98 31 33522055*

In the present work, the micro- spherical SnO_2/Zn_2SnO_4 using a refluxing method were synthesized. The sample was characterized by X-ray diffraction (XRD), UV-Vis. spectrophotometer and field emission scanning electron microscopy (FE-SEM). The photocatalytic activity of the samples *via* decolorization of two dye mixture-methylene blue (M.B.) and methyl orange (M.O.) was examined.

2. Experimental procedure

2. 1 Materials and method

$SnCl_2$. $2H_2O$, NaOH, ZnO powder and Ethanol were used to prepare the samples. All the analytical chemicals were purchased from Merck company. The detailed synthesis procedure is as follows:

3.38 g of $SnCl_2.2H_2O$ was dissolved in 50 mL ethanol and 0.5 g ZnO powder was added in the solution under vigorous stirring. After that, 70 mL (0.1 M) NaOH solution was added drop wise into the above suspension. The resulting mixture was transferred into a flask and refluxed for 8 hours at 180 ºC. Finally, the product was separated by decantation, washed with double distilled water several times and dried. Then, heat treatment of the product was carried out at 500 and 900 ºC for 1 h.

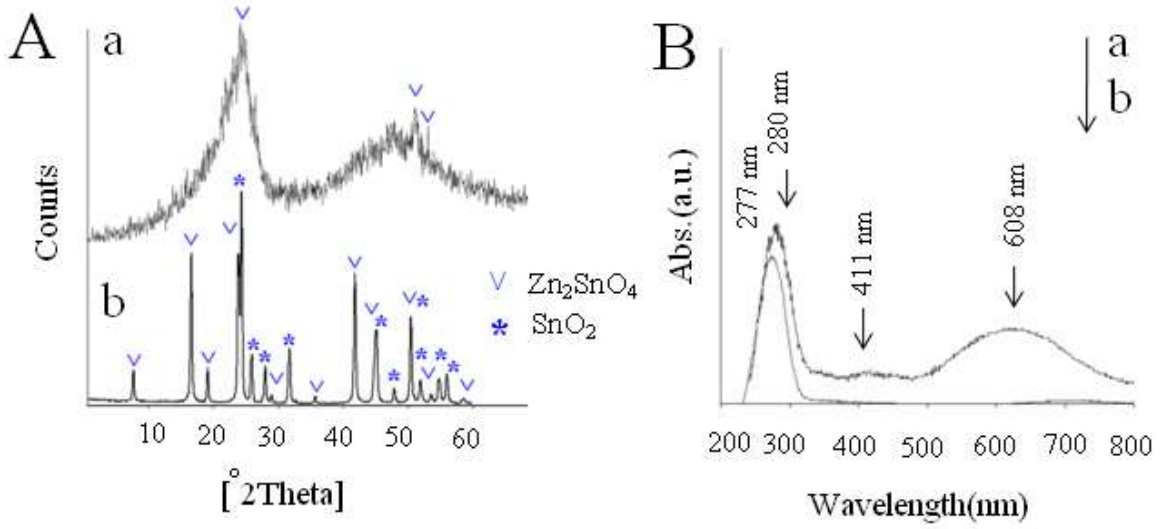

Fig. 1. The XRD patterns (A) and UV-Vis. absorption spectra (B) of the (a) amorphous and (b) SnO_2/Zn_2SnO_4 samples.

2. 2 Photocatalytic experiments

In this study the mixture of methylene blue (M.B.) and methyl orange (M.O.) solution was chosen as an environmental pollutant model. Our goal of choosing above dyes mixture was for the λ_{max} to be separated from each other. The disappearance of peak at λ = 466 nm and λ = 664 nm was chosen for monitoring of dye decolerization for (M.O.) and (M.B.) solutions respectively. In each experiment, 0.10 g of the sample prepared as photocatalyst was added in 200 ml of the mixture of M.B. and M.O. dyes solution (5 mgL^{-1} with respect to each component) with a V/V ration of 1:1. During the experiment, agitation was maintained by a magnetic stirrer to keep the suspension homogeneous. Air was blown into the reaction vessel by an aquarium pump to maintain the solution saturated with oxygen. In this research, a high pressure mercury lamp, 400 W, manufactured by Holland Philips, was used as the light source. Then, the degree of photo decolorization (X), as a function of time, is given by $X = (C_\circ - C)/C_\circ$, where, $C_\circ$ is the initial concentration of dye, and C is the concentration of dye at time t. The progress of photocatalytic decolorization was measured by a UV-Vis. spectrophotometer (Shimadzu UV-2550).

3. Results and discussion

The structure and morphology of the product were characterized by using XRD (Holland Philips Xpert, X-ray diffractometer with Cu-Kα radiation) and field emission scanning electron microscope (FE-SEM), Hitachi S-4160. Fig. 1A(a) shows the broad XRD pattern of the amorphous sample by heat treatment at 500 ºC. XRD result in Fig. 1A(b) revealed that SnO_2/Zn_2SnO_4 (SnO_2, tetragonal, JCPDS No. 88-0287 and Zn_2SnO_4, cubic, JCPDS No. 24-1470) composite was formed after heat treatment at 900 ºC for 1h. In XRD pattern of the SnO_2/Zn_2SnO_4 thermally treated at 900 ºC extremely sharp diffraction peaks was observed which can be related to high crystallinity. Fig. 1B presents UV-Vis. spectra of the prepared samples at 500 and 900 ºC. According to the results for amorphous and SnO_2/Zn_2SnO_4 samples absorbance peaks at about (280, 411, 608 nm) and (277 nm) were observed respectively.

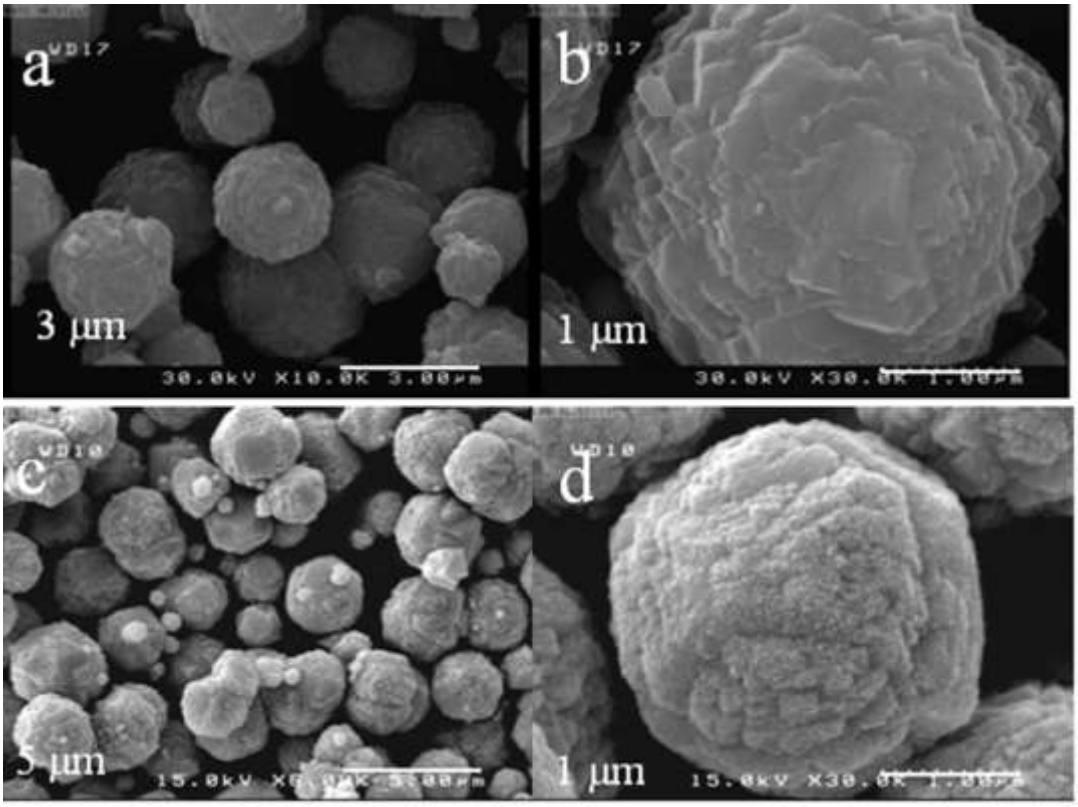

Fig. 2. The SEM images of (a, b) amorphous and (c, d) SnO_2/Zn_2SnO_4 samples.

The UV-Vis. Spectrum result shows the SnO_2/Zn_2SnO_4 sample has a good Crystallinity. Fig. 2(a-d) indicates that the amorphous and SnO_2/Zn_2SnO_4 samples are micro- spherical in morphology with an average diameter of ~2.7 µm and surface of the micro- spheres is not smooth. The photocatalytic activity of the samples was evaluated by decolorization of two dye mixture. The photo decolorization extent of the two dye mixture in the presence of the prepared samples was measured spectrophotometrically at the their respective λ_{max} values. Before photocatalytic experiments, the surface adsorption extent of both (M.O.) and (M.B.) dyes on the surface of the prepared samples was measured in dark condition. Fig. 3 shows the UV-Vis. spectra changes during the adsorption and photo decolorization experiments. The results show that the adsorption extent of (M.O.) and (M.B.) dyes on the surface of the prepared samples was respectively determined about 10, 33 (%) for amorphous sample and 11, 55 (%) for SnO_2/Zn_2SnO_4 sample after 180 min contact time. These results show that, the adsorption of M.O. dye on the surface of the samples is poor. Fig. 4 shows the plots

of photodecolorization percentage versus time for the two dye mixture in presence of samples. Result show that the decolorization extent of (M.O.) and (M.B.) dyes on the surface of the samples was respectively determined about 73, 93 (%) for amorphous sample and 89, 53 (%) for SnO_2/Zn_2SnO_4 sample after 180 min. Perhaps, a reason for the more slightly photocatalytic activity of the amorphous sample is ascribed to the strong absorption at about 608 nm on visible spectrum reign and this absorption is probably should be derived oxygen vacancy in the Zn_2SnO_4 lattice [14, 15]. The fact that the heat treatment sample at 500 ºC exhibited higher activity than the treatment samples at 900 ºC can be related to better visible light absorption and crystalline defects. In summary, the result shows micro-spherical SnO_2/Zn_2SnO_4 is a good candidate for removal of the two dye mixture- methylene blue (M.B.) and methyl orange (M.O.) in aqueous solution.

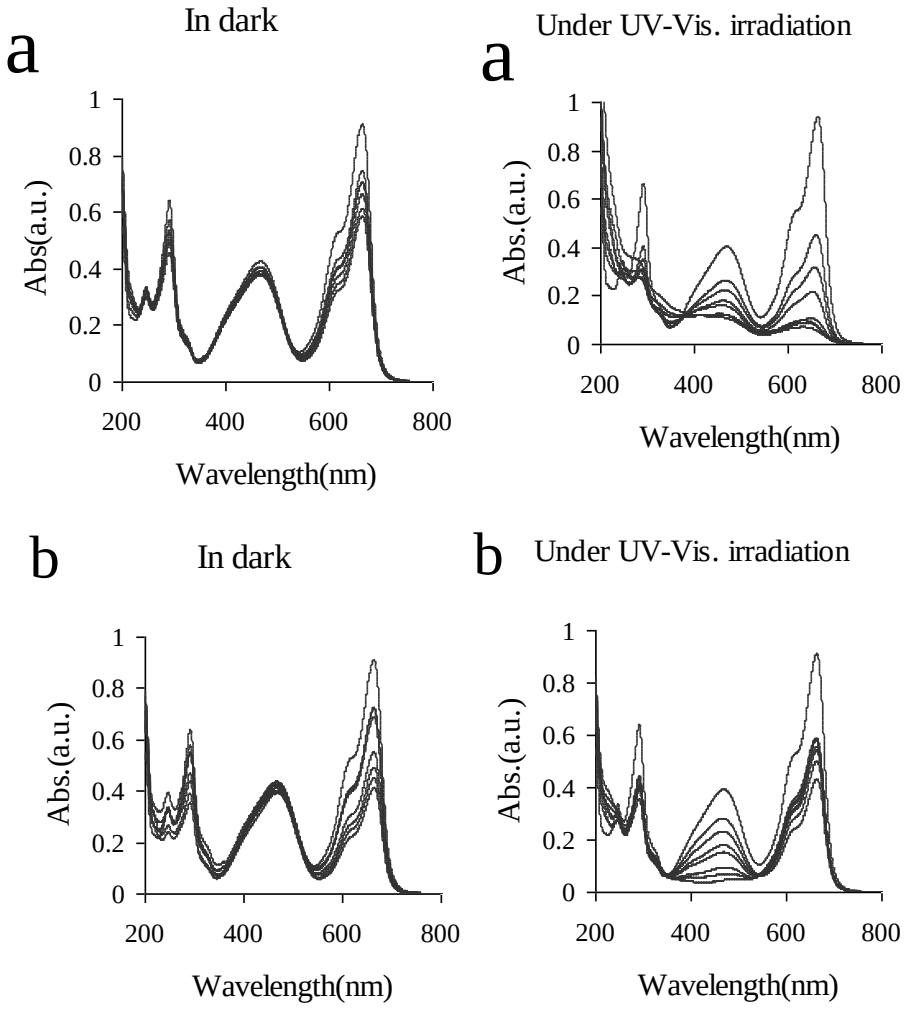

Fig. 3. UV-Vis. spectra changes of a two dye mixture- methylene blue (M.B.) and methyl orange (M.O.) solution in the presence of (a) amorphous and (b) SnO_2/Zn_2SnO_4 samples in dark and under UV-Vis. irradiation conditions.

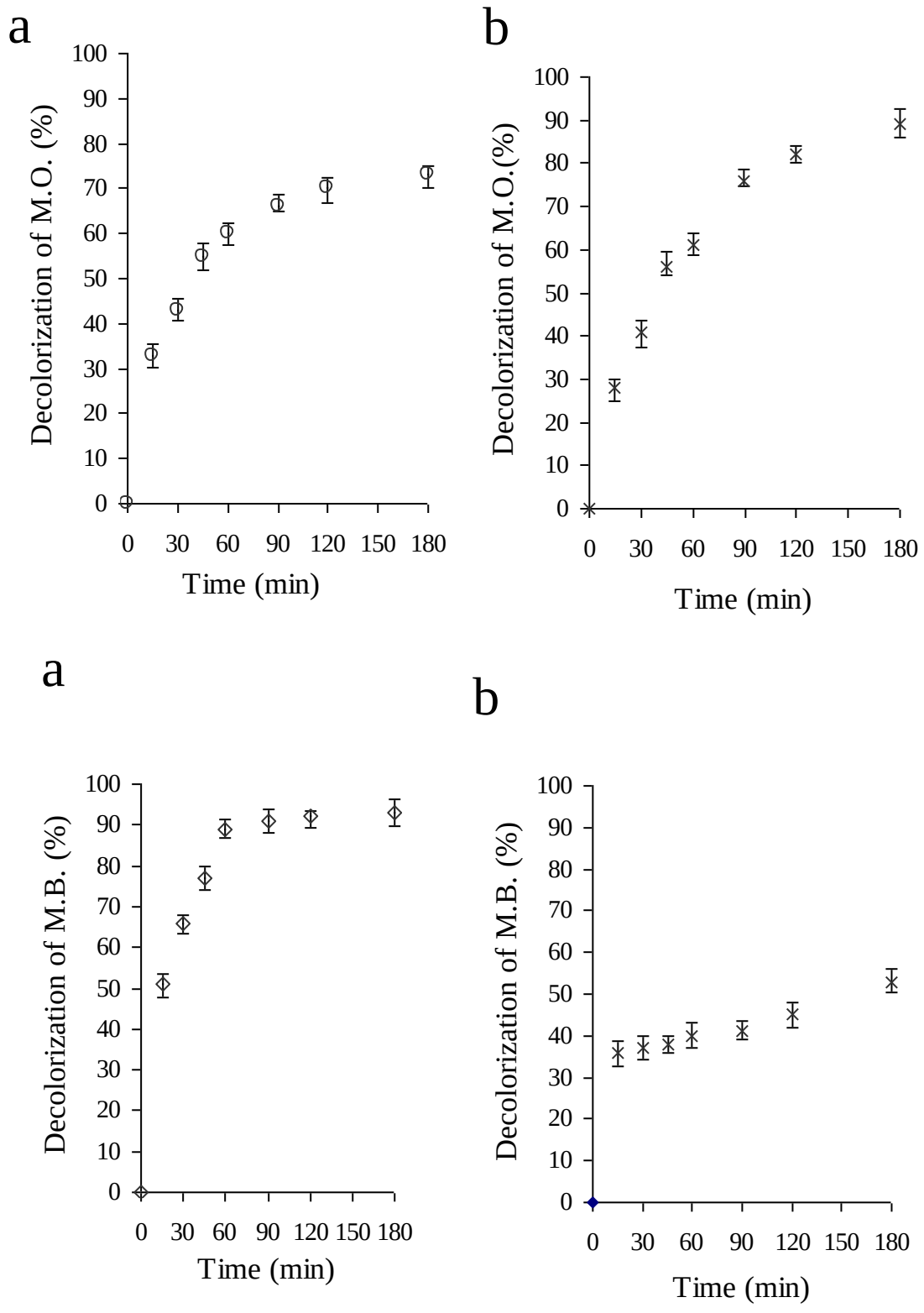

Fig. 4. The plots of photodecolorization percentage of two dye mixture- methylene blue (M.B.) and methyl orange (M.O.) solution versus time in the presence of (a) amorphous and (b) SnO_2/Zn_2SnO_4 samples.

The reusability of the SnO_2/Zn_2SnO_4 sample was investigated through 4 cycles of experiments for decolorization of a mixture of M.B. and M.O. dyes solution. The reusability of the sample after four consecutive uses was obtained to be 98, 95, 90, 90 % (Fig. 5).

4. Conclusion

In conclusion, a simple refluxing method is presented for synthesis of the new micro- spherical SnO_2/Zn_2SnO_4. The SnO_2/Zn_2SnO_4 sample was obtained after heat treatment at 900 ºC. The average diameter of micro- spheres is of about ~2.7 µm. The results indicate that the SnO_2/Zn_2SnO_4 is an efficient photocatalyst for the decolorization of a mixture of M.B. and M.O. dyes solution.

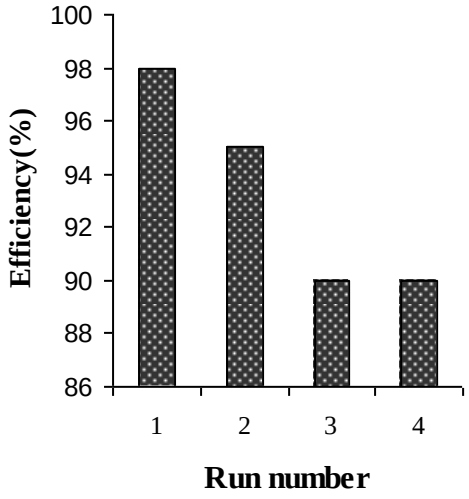

Fig. 5. The reusability of the SnO_2/Zn_2SnO_4 sample after four consecutive uses.

Acknowledgments

We are grateful to Payame Noor University for its financial support.

References

[1] J. Li, M. Yang, Z. Feng, F. Lan, C. Teng, D. Li, J. Tang, Mater. Lett., 161 (2015) 591-594.

[2] Y.J. Shin, C.C. Su, C.W. Chen, C.D., Dong, Catal. Commun., **72** (2015) 127-132

[3] X. Xu, S. Li, X. Wang, Y. Ma, X. Wang, K. Gao, Mater. Lett., **143** (2015) 75-79.

[4] J. Liu, S. Zuo, L. Yu, Y. Yu, B. Li, P. Chen, Particuology, **11** (2013) 728-731.

[5] J. Huang, S. Liu, L. Kuang, Y. Zhao, T. Jiang, S. Liu, X. Xu, J. Environ. Sci., **25** (2013) 2487-2491.

[6] M. Hojamberdiev, K.I. Katsumata, K. Morita, S.A. Bilmes, N. Matsushita, K. Okada, Appl. Catal. A., **957** (2013) 12-20.

[7] لادن زمان، رامین یو سفی، محمد نیائی‌فر، مجله علمی–پژوهشی شیمی کاربردی، دوره ۱۰، شماره ۳۶، (۱۳۹۴).

[8] بهار خدادادی، مجله علمی–پژوهشـــی شـــیمی کاربردی، دوره ۸، شماره ۲۷، (۱۳۹۲).

[9] S. Majumdar, Ceramic International, **41** (2015) 14350-14358.

[10] B. Munirathinam, H. Pydimukkala, N. Ramaswamy, L. Neelakantan, Appl. Surf. Sci., **355** (2015) 1245-1253.

[11] L. Qin, S. Liang, A. Pan, X. Tan, Mater. Lett. **141** (2015) 255-258.

[12] P. Junploy, S. Thongtem, T. Thongtem, A. Phuruangrat, Superlattices Microstructures, **74** (2014) 173-183.

[13] Y. Sato, J. Kiyohara, A. Hasegawa, T. Hahori, M. Ishida, N. Hamada, N. Oka, Y. Shigesato, Thin Solid Films, **518** (2009) 1304-1308.

[14] A.A. Firooz, A.R. Mahjoub, A.A. Khodadadi, M. Movahedi, Chem. Engin. J., **165** (2010) 735-739.

[15] J.W. Zhao, L.R. Qin, L.D. Zhang, Solid State Commun., **141** (2007) 663-666.